

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 December 2001 (13.12.2001)

PCT

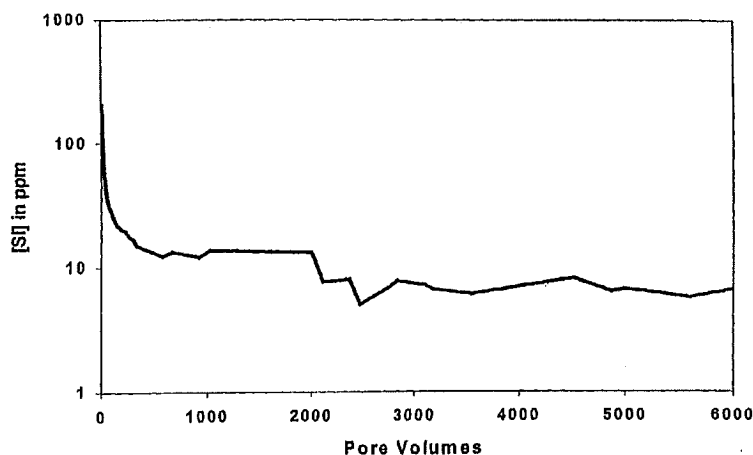
(10) International Publication Number
WO 01/94744 A1

- (51) International Patent Classification⁷: **E21B 37/06**,
43/25, 41/02, 43/267 (GB). **BOURNE, Hugh, Malcolm** [GB/GB]; 1 Turnberry
Drive, Inverurie, Aberdeenshire AB51 3WT (GB).
- (21) International Application Number: PCT/GB01/02482 (74) Agent: **MURGITROYD & COMPANY**; 373 Scotland
Street, Glasgow G5 8QA (GB).
- (22) International Filing Date: 6 June 2001 (06.06.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0013603.6 6 June 2000 (06.06.2000) GB
0020137.6 17 August 2000 (17.08.2000) GB
- (71) Applicant (for all designated States except US): **T R OIL
SERVICES LIMITED** [GB/GB]; Howe Moss Place,
Kirkhill Industrial Estate, Dyce, Aberdeen AB2 0GL
(GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,
TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (72) Inventors; and
(75) Inventors/Applicants (for US only): **HEATH, Stephen,
Mark** [GB/GB]; 15C Dee Street, Aberdeen AB11 6AW
- Published:
— with international search report

[Continued on next page]

(54) Title: MICROCAPSULE WELL TREATMENT

Scale Inhibitor Release Profile from a Plastic Capsule



(57) Abstract: A material and a device for releasing chemicals in a fluid environment is disclosed, and a method for releasing substances into downhole fluid environments. The invention also relates to materials for sand control and hydraulic fracturing. The substance release device typically comprises a polymeric material for releasing a substance into a downhole fluid environment in a well, and in preferred embodiments the material comprises a spherical, plastic chemical release capsule which is hard, permeable and may encapsulate a range of solids and/or liquids for subsequent release. These solids or liquids can include inhibitors such as scale inhibitors and other oilfield production chemicals for release into the wellbore of an oil or gas producing well or a water injection well.

WO 01/94744 A1



— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

microcapsule well treatment

1

2

3 This invention relates to material for releasing
4 chemicals in a fluid environment, and to a method of
5 producing the material. In particular, this invention
6 relates to materials for sand control and hydraulic
7 fracturing, the same materials releasing chemicals in
8 a fluid environment, and to a method of producing
9 these materials.

10

11 Advances in drilling and completion technology have
12 revolutionised new field development and in-fill
13 drilling strategies. The use of subsea and/or
14 horizontal well completions is now common and in some
15 cases these complex wells require sand control
16 measures to be installed to maintain the integrity of
17 the wellbore and prevent it collapsing. A variety of
18 well completions are conventionally used for sand
19 control purposes including fracture packing and
20 gravel-packing techniques, prep-packed screens, wire

1 wrapped screens and expandable screens. It is
2 preferred that the flow of fluids through the sand
3 control system is not impaired since this can reduce
4 the productivity and/or injectivity of the well.
5 Hydraulic fracturing is used to improve well
6 productivity. It is therefore preferred that the flow
7 of fluids into and through the propped fracture is
8 not impaired since this can also reduce the
9 productivity and/or injectivity of the well.
10
11 The installation of subsea and/or horizontal well
12 completions also increase the complexity, logistical
13 difficulty and cost of intervention for the
14 mitigation of production chemistry problems such as
15 inorganic scale formation, asphaltene and wax
16 deposition, corrosion and bacterial growth on the
17 wellbore conduits.
18
19 According to the present invention there is provided
20 a substance release device comprising a polymeric
21 material for releasing a substance into a downhole
22 fluid environment in a well.
23
24 In preferred embodiments the material comprises a
25 spherical, plastic chemical release capsule which is
26 hard, permeable and may encapsulate a range of solids
27 and/or liquids for subsequent release. These solids
28 or liquids can include inhibitors such as scale
29 inhibitors and other oilfield production chemicals
30 for release into the wellbore of an oil or gas
31 producing well or a water injection well.

1 The material can be used for sand control and for
2 hydraulic fracturing (for clarity the material shall
3 ~~herein be termed "a proppant" when it is applied to~~
4 hydraulic fractures) and well clean up. The material
5 can be used for sand control purposes whilst also
6 providing controlled release of oilfield production
7 chemicals from within the sand control medium. This
8 includes application in gravel packed, fracture
9 packed and pre-packed screen sand control systems.
10 The material can also be used for more effective well
11 clean up after completion in both injection and
12 production wells via the controlled release of enzyme
13 based materials that release acids to dissolve any
14 mineral deposits and breakdown residual bio-polymers
15 from the well completion process. The material can
16 be used for hydraulic fracturing purposes whilst also
17 providing controlled release of oilfield production
18 chemicals from within the proppant medium. In
19 addition this material may be used for hydraulic
20 fracturing and either or both the controlled release
21 of oilfield chemicals and proppant flow back control.
22 The material may also be used within the rathole of a
23 well to provide controlled release of an oilfield
24 chemical into the aqueous environment.

25
26 Preferably the polymeric material is used for sand
27 control and hydraulic fracturing.

28
29 Preferably the polymeric material is permeable.

30

1 The material can comprise a polymeric plastics
2 material such as polypropylene, polyethylene, high
3 density polyethylene, high density polypropylene,
4 polyethylene terephthalates, polyamides (both
5 aliphatic and aromatic), liquid crystal polymers,
6 liquid engineered resins, starch and polyhydroxy
7 alkanoates or mixtures of these.

8
9 The material typically comprises a matrix that
10 provides the material with support, and which
11 contains the chemical to be released.

12
13 Other materials may be used as the matrix such as
14 acrylic, polybutylene, polycarbonate, polyester,
15 polystyrene, polyurethane, polyvinyl chloride,
16 polycaprolactone, polybutylene terephthalate,
17 polyvinyl alcohol, polylactic acid, polyglycolide,
18 polyester amide, polyimides, acrylonitrile-butadiene-
19 styrene, acrylonitrile-styrene-acrylate,
20 polyoxymethylene, polybutylene, polyisobutylene,
21 polyvinylbutyral, epichlorohydrin elastomer, nitrile
22 elastomer, nitrile rubber, polyetherketone,
23 polyetheretherketone, polyetherketoneketone,
24 polymethylmethacrylate, polyethylene oxide,
25 polyphenylene oxide, polysulphones,
26 polyethersulphone, polyurea, chlorinated
27 polyethylene, ethylene-chlorofluoroethylene,
28 tetrafluoroethylene-perfluoropropylene,
29 Perfluoroalkoxy, silicon rubbers and other polymeric
30 materials consisting of mixtures of the above and
31 copolymers, terpolymers and

1 hydrophobically/hydrophilically modified and
2 crosslinked derivatives of the above.

3
4 Other materials can be used instead of or in addition
5 to the polymeric or plastics material, such as
6 thermoplastic rubber, resins, hot melt adhesives,
7 fibreglass, silicones, fluorosilicones e.g. Ryton,
8 polysiloxanes, fluoroelastomers e.g. Viton, Aflas,
9 fluorocarbons e.g. PTFE, PVDF, halogenated polymers,
10 cellulose, polysaccharides, lignin, chitin, gums and
11 mixtures and derivatives of the above.

12
13 In addition waxes, calcium stearate, and metallocene
14 can be used instead of or in addition to the
15 polymeric or plastics material.

16
17 The material contains a high active content of scale
18 inhibitor, or the chemical to be released, typically,
19 10-90wt%/v. The high mass of inhibitor contained
20 within the capsule can reduce (and on some wells
21 potentially eliminate) the need for scale related
22 intervention. In addition, the high loading of
23 inhibitor offers the potential for significant
24 treatment lifetime with minimal product deployment.

25
26 The release of the scale inhibitor can be further
27 controlled by changing its solubility in the brine
28 phase or by restricting contact between the inhibitor
29 salt and the brine phase. The solubility of the
30 inhibitor in the brine phase can be reduced by
31 increasing the ratio of the polyvalent cation to

1 inhibitor in the precipitated salt or by changing the
2 nature of the polyvalent cation. Careful selection
3 of the polymer type or the use of hydrophobic
4 additives can reduce water ingress into the porous
5 matrix and thus reduce inhibitor release.

6
7 In certain embodiments the hardness of the material
8 can be varied by changing the chemical composition of
9 the polymer plastic matrix and/or cross-linking the
10 polymer plastic material or by reinforcing the
11 particle matrix with natural, synthetic, glass or
12 metal fibres, sand, silicates or other minerals and
13 ceramic matrices such as bauxite, resins, carbon or
14 boron based materials and impact modifiers. Typically
15 the unconfined compressive strength would be in the
16 range 500-100,000psi.

17
18 In other embodiments the material can be selected to
19 have an oil tolerance which can be adjusted by
20 changing the chemical composition of the polymer
21 plastic matrix and/or modifying the hydrophobic or
22 hydrophilic properties of the polymer matrix or
23 cross-linking the polymer matrix with a suitable
24 reagent. In addition, the chemical resistance to
25 acids and oil may be increased by the addition of a
26 chemical stabiliser, for example Ebonite.

27
28 The capsules are typically of permeable polymeric
29 material, and are manufactured using an underwater
30 pelletising system consisting of an extrusion and
31 either a spheronisation or granulation process. The

1 capsules typically contain a high active content of
2 scale inhibitor, typically, 10-90wt%/v. The
3 particles can be produced over a wide range of sizes.
4 The size distribution of the particles in a sample of
5 material can be large, with a heterogeneous
6 distribution of particles of different sizes, or
7 small, with a fairly homogeneous range of similarly
8 sized particles (so called mono dispersed particles).
9 The range of preferred sizes is typically 250µm -
10 5mm, with the distribution of size being typically
11 ±5% of the mean size.

12

13 The density of the capsules can be controlled by the
14 variation of the type of polymer matrix and/or by
15 including a weighting agent such as barite, zirconium
16 oxide, manganese oxide, titanium dioxide, tungsten or
17 magnetite. The hardness, compressive strength and
18 elastic properties (rigidity and
19 elongation/deformation) can be controlled by the
20 variation of the type of polymer matrix and/or
21 including a strengthening agent such as glass, sand,
22 minerals, carbon or boron fibres and/or an impact
23 modifier. The unconfined compressive strength is
24 typically between 500-100,000psi.

25

26 The material is typically extruded from a pelletising
27 system. A single or twin screw system can be used,
28 and other mixers such as Farrell and Banbury mixers
29 or a Feeder extruder can be used.

30

1 Mono dispersed spherical particles (i.e. a relatively
2 homogeneous mixture of similarly sized particles) can
3 be produced over a wide range of particle size,
4 typically 250 μ m - 5mm, with the distribution of size
5 being typically $\pm 5\%$ of the mean size. The variation
6 in particle size can allow certain embodiments of the
7 invention to provide gravel packs of different mesh
8 sizes, where in certain embodiments there is an
9 advantage in having a narrow range of particle sizes
10 in the one application. The spherical and mono
11 dispersed nature of the particles typically provides
12 better packing in the gravel pack and a more uniform
13 pore throat size. This can provide more effective
14 sand control and reduce the turbulence in the pore
15 throats, thus improving the gravel pack permeability.

16

17 In certain embodiments, the material can have a low
18 and adjustable density (specific gravity usually
19 between 0.9 and 2.0 where mostly polymeric materials
20 are used, and even higher SG values up to 12 can be
21 achieved with a higher proportion of heavier
22 materials e.g. mostly tungsten) and that can be
23 adjusted by changing the chemical composition of
24 polymeric matrix and/or by adding a weighting agent
25 such as barite, tungsten, zirconium oxide or
26 magnetite or any other material denser than the
27 polymer. The optional low density of the material
28 can provide more effective gravel pack placement and
29 simplify the gravel-packing operation, especially in
30 deviated wells because the high viscosity fluids
31 normally needed to carry dense proppant and/or gravel

1 pack material through a pipeline system will not be
2 needed.

3
4 In certain embodiments, typically for application in
5 rat holes, the polymer matrix can slowly degrade over
6 a time period of 1 week to 10 years leaving little or
7 no residue. This will typically enable re-treatment
8 of the product into the rathole once the product has
9 degraded. The lifetime of the plastic capsule can be
10 adjusted by changing the chemical composition and
11 molecular weight of the polymeric matrix and/or
12 incorporating a dissolution agent such as heavy
13 aromatic naphthas, peroxides, per sulphates, enzymes
14 and metal oxide catalysts into the spherical plastic
15 capsule. The rate and lifetime of release of the
16 encapsulated chemical can be controlled such that it
17 corresponds to the degradation lifetime of the
18 polymer matrix material. This may be achieved by
19 varying the amount of encapsulated chemical in the
20 polymer matrix material, changing the chemical
21 composition of the polymer matrix and the inhibitor
22 salt or by coating the polymer matrix and/or coating
23 the encapsulated inhibitor salt.

24
25 In certain embodiments, for application in gravel
26 packs and hydraulic fractures, the polymeric material
27 is preferably somewhat pliable so that it can display
28 a slight amount of deformation at the point of
29 contact, increasing the surface area of contact
30 between particles. In gravel packs and hydraulic
31 fractures this reduces the effect of applied stress

1 and can result in improved sand and proppant flowback
2 control respectively. The amount of deformation of
3 the polymer matrix required to control sand
4 production and proppant flowback can be adjusted by
5 changing the chemical composition of the matrix
6 and/or including a strengthening agent such as glass,
7 sand, minerals, carbon or boron fibres and/or an
8 impact modifier. Laboratory data from stressed
9 cyclic flow back tests with mixtures of conventional
10 proppant and chemically impregnated conventional
11 porous proppant had indicated that although these
12 mixtures passed the initial conductivity tests the
13 proppant pack collapsed under cyclic stress and
14 flowed out of the test apparatus. However, when the
15 same tests were repeated with mixtures of
16 conventional proppant and this polymeric material no
17 proppant flow back was observed. This was
18 attributed to cohesion of the proppant pack induced
19 by the flowback control characteristics of the
20 polymeric material.

21
22 Most preferred embodiments of the material comprise
23 spherical capsules although other shapes may be in
24 accordance with the invention. Spherical capsules
25 have the additional advantage for gravel pack
26 applications in that they can be packed more
27 efficiently into a defined space than other shapes of
28 material. In addition, the use of a more homogeneous
29 particle size typically leads to the formation of
30 more homogeneous pore throats. This can afford the
31 gravel pack more effective sand control

1 characteristics and can reduce the turbulence within
2 the sand or proppant pack, which may lead to an
3 increased effective permeability.

4
5 In preferred embodiments of the invention the
6 material is charged with any scale inhibitor suitable
7 for the purpose of inhibiting scale in a well bore
8 formation. This may include water soluble organic
9 molecules with carboxylic acid, aspartic acid, maleic
10 acids, sulphonic acids, phosphonic acid and phosphate
11 esters groups including copolymers, ter-polymers,
12 grafted copolymers and derivatives of the above.
13 Examples of such compounds include aliphatic
14 phosphonic acids such as diethylene triamine penta
15 (methylene phosphonate) and polymeric species such as
16 polyvinylsulphonate. The scale inhibitor can be in
17 the form of the free acid but is preferably in the
18 form of mono and polyvalent cation salts such as Na,
19 K, Al, Fe, Ca, Mg, NH_4 .

20
21 The chemicals can be solid and mixed with the matrix
22 to give a generally homogeneous mixture comprising
23 the plastics matrix and the chemical. Alternatively,
24 the scale inhibitors etc can be encapsulated in
25 liquid form e.g. by being immobilised, absorbed or
26 encapsulated in an appropriate matrix such as a
27 diatomised clay, resin, starch or other
28 polysaccharide material, polyvinyl alcohol and super-
29 adsorbing polymers and then being incorporated in
30 solid form into the main product matrix.

31

1 The material can contain scale inhibitor in most
2 preferred embodiments but instead in other
3 embodiments either no chemical is included in the
4 formulation or a wide range of other oil field
5 chemicals such as inhibitors can be carried including
6 but not limited to corrosion inhibitors, biocides,
7 wax and asphaltene control chemicals, pour point
8 suppressants, dispersants, hydrate and halite
9 inhibitors, demulsifiers, gel breakers, tracers, drag
10 reducers and well clean up chemicals including
11 enzymes. These can also be encapsulated in either
12 solid or liquid form into the material.

13

14 Certain embodiments of the present invention tackle
15 sand and combined sand/scale control in gravel packed
16 and pre-packed screen wells by using a hard,
17 permeable, spherical plastic capsule, optionally
18 carrying a chemical substance such as an inhibitor, ,
19 although other embodiments can simply provide an
20 alternative material to sand or gravel for use in
21 gravelpacks. The plastic capsule can be manufactured
22 using a hot melt extrusion and spheronising process
23 and can optionally contain approximately 10-90wt% of
24 active scale inhibitor and can benefit from a low and
25 adjustable density. The high mass of inhibitor
26 contained within the particle can reduce the need for
27 scale-related intervention and offers the potential
28 for significant treatment lifetime. The low density
29 of the particle also aids placement and simplifies
30 the gravel packing operation. In addition, the
31 spherical nature and mono dispersed characteristics

1 of the plastic capsule can provide more effective
2 packing and a uniform pore throat size for the gravel
3 pack. This can provide improved sand control and
4 increase the pack permeability through reduced
5 turbulence at pore throats. The provision of a
6 material for sand and/or combined sand/scale control
7 in e.g. gravel packed and pre-packed screen wells
8 comprising a hard, optionally permeable material with
9 or without a loading of chemical to be delivered to
10 the well is another aspect of the present invention,
11 typically where the material comprises a number of
12 particles having a narrow size range e.g. 400um+/-5-
13 10%.

14

15 The invention also provides a method of treating a
16 well, the method comprising loading a substance into
17 a polymeric material, inserting the material into the
18 well, and allowing the substance to leach from the
19 polymeric material into the well.

20

21 Typically the material is inserted into a fissure,
22 fracture, screen area, gravel pack, fracture pack or
23 a pre-packed screen, usually as part of the well
24 completion.

25

26 The invention also provides a method of forming a
27 chemical-releasing particle for release of chemicals
28 in a fluid environment, the method comprising mixing
29 the chemical to be released with a matrix material
30 forming the particle, and thereafter forming the
31 particle (e.g. by melting, mixing and/or extrusion of

1 the mixture) from the mixture of the matrix and the
2 chemical, so that the chemical is dispersed
3 (preferably homogeneously) throughout the formed
4 particle.

5
6 In an extruder system, the polymeric matrix material
7 and the other additives are typically fed into the
8 top of the extruder via a hopper at the rear of the
9 extruder system. The extruder is preferably an auger
10 type mixer, which is typically heated to melt the
11 polymer matrix. The auger screw system then
12 typically mixes and disperses the other additives in
13 the molten polymer as the mixture typically moves
14 along the auger screw. Typically a vent is provided
15 before the material reaches the head of the extruder
16 to allow gas or moisture to escape. However this
17 venting can be further enhanced by fitting a vacuum
18 pump to more effectively withdraw gas and moisture.
19 The mixture typically proceeds into a throat which
20 typically slows down the mixture and typically
21 increases the pressure before typically releasing the
22 mixture in the form of strands of typically circular
23 cross section that are extruded through apertures in
24 an extrusion head. The strands are then typically
25 cooled in a water bath and typically pelletised into
26 cylindrical pellets using a chopper. The temperature
27 of the heated extruder screw is normally dependent on
28 the melting point of the polymers, but the typical
29 extrusion temperatures vary between 100°C and 400°C.
30

1 The invention also provides a polymeric downhole
2 proppant.

3
4 The invention also provides a method of supporting a
5 well or a portion thereof, comprising disposing a
6 support material in the well or portion to be
7 supported, wherein the support material comprises a
8 polymeric material.

9
10 The invention also provides a polymeric material for
11 use downhole for the control of particulate matter
12 entering the production stream of the well.

13
14 The invention also provides a method of controlling
15 the entry of particulate matter into the production
16 stream of a well, the method comprising disposing a
17 number of polymeric devices into the wellbore between
18 the formation and the production fluids outlet of the
19 well.

20
21 Examples of the present invention will now be
22 described by way of illustration only and with
23 reference to the accompanying figures, wherein

24
25 Fig. 1 is a schematic representation of
26 apparatus for producing devices according to the
27 invention;

28 Fig. 2 is a graph plotting the concentration of
29 scale inhibitor against the number of cycles of
30 fluid passing through a closed system;

1 Figure 3 shows the plot of compressive stress
2 (psi) versus axial strain for certain
3 embodiments of devices;
4 Figure 4 shows a graph of pore throat size
5 distribution versus gravel pack compressive
6 stress as determined from a mercury stress
7 injection test on a further embodiment;
8 Fig 5 shows a thin section photomicrograph of a
9 sand slurry injection test of a further
10 embodiment;
11 Fig 6 shows a graph of the % weight loss of
12 total material and scale inhibitor versus the
13 degradation time of the another embodiment of
14 material in days at 107°C; and
15 Fig 7 shows scale inhibitor release profile
16 under simulated rathole conditions for PHA
17 polymer in produced brine at 107°C in another
18 embodiment.
19
20 To form the capsules an underwater pelletising
21 process is used, which utilises an extruder having
22 either a single screw or twin screw system. A single
23 screw extruder comprises a steel tube of variable
24 length, which has one single shaft screw that rotates
25 at speed in the tube as it is heated, melting the
26 polymer and mixing it as it is pushed down the tube.
27 A twin screw extruder consists of two co-rotating
28 screws in a single barrel with a variety of mixing
29 zones down the length of the heated barrel in which
30 both screws work together to mix and blend. This
31 works the material more effectively compared with a

1 single screw extruder and a better dispersion of the
2 solid additives into the polymer is achieved.

3
4 The dispersion of the material additives into the
5 binder or polymer can be divided into four steps:

- 6
7 (a) wetting of the additives = pre-mixing of the
8 additives with the binder;
9 (b) dispersion of agglomerates into aggregates and
10 primary particles;
11 (c) distribution into the binder or polymer;
12 (d) stabilisation against re-agglomeration.

13
14 The plastic/chemical mix is then introduced into a
15 known underwater pelletising system shown in Fig. 1.
16 The Fig. 1 system is suitable generally for producing
17 pellets according to the invention.

18
19 The pre-extruded cylindrical pellets or the polymeric
20 matrix material and additives for example inhibitors
21 and weighting agents are fed via a hopper into an
22 extruder or melt pumps which force the molten mixture
23 through a screen changer and/or polymer diverter
24 valve, which helps build up the pressure at the head,
25 and for the start-up of the run. A gear pump can be
26 used to regulate the flow of polymer to the head to
27 keep the pressure evenly distributed throughout the
28 system. The mixture then flows through a die 10
29 having a series of holes arranged in a circular
30 pattern. As the mixture emerges from the holes, it
31 is cut into lengths by rotating blades 12 and is

1 solidified into pellets by process water which is
2 pumped through conduits 15 across the material face
3 in the cutting chamber 17. Tempered water transfers
4 the pellets via conduits 20 to a centrifugal dryer
5 and spheroniser 22 where the water and the pellets
6 are separated and the dry spherical pellets are
7 discharged via chute 25. The process water is
8 filtered, pressurised, tempered and returned to the
9 Cutting chamber 17. The system can produce pellets
10 (e.g. mono dispersed pellets) typically at between 10
11 to 6000kg/hr in a size range typically from 40µm to
12 5mm ±5%.

13
14 The extrusion process may be combined with a Farrell
15 bridge consisting of two mixing areas. In the first
16 area the mixture is melted and mixed in an upper
17 chamber using single screw, before it is dropped down
18 to two co-rotating screws in the bottom chamber,
19 where further mixing of the product occurs before it
20 is delivered to the head of the chamber. A venting
21 process takes place between the top and bottom
22 chambers to remove any moisture. This venting
23 process can be enhanced by use of a vacuum pump
24 system.

25
26 A hole may be cut into the side of the extruder,
27 usually two-thirds of the way down the barrel and it
28 is used to feed additives and fillers directly into
29 the barrel, commonly termed a feeder extruder.

30

1 An oil-heated drum mixer or Banbury Mixer may be used
2 to slowly turn and blend the polymers and additives.
3 The additives usually need to be more thermally
4 stable and the mixing process is much slower.
5
6 The spherical plastic capsule may have a variable oil
7 tolerance which can be adjusted by changing the
8 chemical composition of the polymer plastic matrix
9 and/or modifying the hydrophobic or hydrophilic
10 properties of the polymer plastic matrix or cross-
11 linking the polymer plastic matrix with a suitable
12 reagent. To modify the polymer a thermally stable
13 hydrophobic group such as an aliphatic or an aromatic
14 amide, lauryl or phosphate ester, or any other
15 hydrophobic group is grafted onto the polymer
16 backbone as a side chain. This provides the polymer
17 with improved oil or water resistance depending on
18 the nature of the polymer matrix and the modification
19 process. In the cross-linking process, the polymer
20 molecules are linked using peroxide, silanes and
21 metallocene chemicals to form a more complex
22 macromolecular structure. This is then cured at
23 various temperatures to achieve improved strength and
24 oil, water, acid and bacterial resistance.
25
26 The scale inhibitors may be encapsulated in liquid
27 form if they are immobilised on an appropriate matrix
28 such as a diatomised clay, resin, super-adsorbing
29 polymer and high porosity versions (~40-50%) of the
30 main polymer matrix material. In the immobilisation
31 process a liquid is incorporated into a solid matrix

1 by a spray drying, shear mixing, emulsion
2 polymerisation, coating or by a simple soaking
3 process in which the liquid is either imbibed into or
4 adsorbed onto the surface of the solid material.

5
6 Coatings can be applied to the outer surfaces of the
7 capsules; for example, organic surfactants and waxes
8 can be added to the polymer melt or applied to the
9 outer surfaces of the resultant particle to achieve
10 improved oil, water, acid and bacterial resistance.
11 In addition, the polymer melt additive or surface
12 coating can also be used to control the release rates
13 of the encapsulated chemical into the wellbore of an
14 oil or gas producer well or a water injection well.

15
16 The resultant spherical particles may be injected
17 into an oil well or water injection well. Certain
18 embodiments of the particles can withstand
19 particularly high pressures associated with such
20 wells. The particles may be injected into the rat-
21 hole, hydraulic fractures or into the annulus in
22 gravel packed, fracture packed and pre-packed sand
23 screen completed wells. The chemicals such as scale
24 inhibitors will gradually over time leak out from the
25 particles and so treat the local environment
26 accordingly. The release rate can be controlled by
27 varying the amount of encapsulated chemical in the
28 polymer matrix material, changing the chemical
29 composition of the polymer matrix and the inhibitor
30 salt or by coating the polymer matrix and/or coating
31 the encapsulated inhibitor salt.

1 Examples .

2

3 **Example 1** -- Extrusion Temperature 165°C - 200°C

4

5 Particles were produced using the above Fig. 1 device
6 and having the following proportion of constituents:-

7

8 40% PP/HDPE (60/40 mix of polypropylene/high density
9 polyethylene) - as the plastic matrix material; The
10 material can be added as a fine powder of average
11 size 0-100µm.

12

13 30% Magnetite (Iron oxide) - as the weighting agent;
14 The material can be added as a fine powder with an
15 average particle size of 1-100µm.

16

17 30% Solid Polycarboxylate - as a scale inhibitor
18 salt. The material can optionally be added as a fine
19 powder with an average particle size of 1-100µm, and
20 typically around 70µm or less.

21

22 The plastic matrix material and the other two
23 components were added into the hopper and fed into
24 the top of the extruder. The mixture was then melted
25 within the heated auger type mixer and the components
26 dispersed in the polymer matrix, as described earlier
27 in the manufacturing process, before being extruded
28 using the underwater pelletising system also
29 described earlier. The finished capsule was
30 particularly suitable for rat hole applications where

1 a weighting agent is normally necessary to keep it in
2 place and prevent it from floating out of position.
3 The specific gravity of this material was ~1.4 and
4 it's unconfined compressive strength was >500psi.
5 The product was also thermally stable in both brine
6 and oil up 140°C. However, above this temperature
7 the product will soften and agglomerate and may break
8 down in crude oil. The scale inhibitor was an
9 optional constituent, and this can be omitted in
10 embodiments intended for gravelpack applications.

11

12 **Example 2** - Extrusion Temperature 165°C - 200°C

13

14 Particles were produced using the above Fig. 1 device
15 and having the following proportion of constituents:-

16

17 60% PP/HDPE (60/40 mix of polypropylene/high density
18 polyethylene) - as the plastic matrix material; The
19 material can be added as a fine powder with an
20 average particle size of 1-100µm.

21

22 2% Tungsten - as the weighting agent; The material
23 can be added as a fine powder with an average
24 particle size of 1-100µm.

25

26 38% Solid Polycarboxylate. The material can be added
27 as a fine powder with an average particle size of 1-
28 100µm.

29

30 This capsule was manufactured as detailed for the
31 previous example. The product is typically suitable

1 for scale control in rat holes. The reduction in the
2 amount of weighting agent in the plastic capsule
3 optionally allows more scale inhibitor to be loaded
4 into the product agent, thus potentially increasing
5 the treatment lifetime. The reduction in the amount
6 of weighting agent also increases the compressive
7 strength. The specific gravity of this material was
8 ~1.20 and its unconfined compressive strength was
9 greater than 1000psi. The product displayed a
10 thermal stability similar to that in Example 1.
11 Again, the scale inhibitor was an optional
12 constituent, and this can be omitted in embodiments
13 intended for gravelpack applications.
14

15 **Example 3 - Extrusion Temperature 200-220°C**
16

17 Particles were produced as described for the previous
18 2 examples and having the following proportion of
19 constituents:-
20

21 50% PP/HDPE (60/40 mix of polypropylene/high density
22 polyethylene) - as the plastic matrix material. The
23 material can be added as a fine powder with an
24 average particle size of 1-100µm
25

26 30% Glass - Strengthening Agent. The material can be
27 added as a fine powder with an average particle size
28 of 1-100µm.
29

30 20% Solid THPS (Tetrakis(hydroxymethyl)phosphonium

1 sulphate) - as a biocide salt. The material can be
2 added as an agglomerate with an average particle size
3 of 50-2000 μ m.
4

5 This capsule was manufactured as detailed for the
6 previous example. The extrusion temperature was
7 slighter higher to ensure the glass which was added
8 as a fine powder was properly dispersed during the
9 extrusion process. The addition of glass strengthens
10 the capsule by up to 10% as well as increasing the
11 oil resistance and thermal stability of the product
12 to over 150°C. The specific gravity of this material
13 was ~1.20. The unconfined compressive strength was
14 1100psi. This capsule can be used for the control of
15 sulphate reducing bacteria to prevent the generation
16 of H₂S and associated corrosion problems.
17

18 **Example 4** - Extrusion Temperature 200°C - 240°C
19

20 Particles were produced as described above for the
21 previous three examples and having the following
22 proportion of constituents:
23

24 80% PET/PP (20/80 mix of polyethylene
25 terephthalate[PET)/polypropylene[PP]) - as the
26 plastic matrix material; the material can be added
27 as a fine powder with an average particle size of 1-
28 100 μ m.
29

1 20% Solid Phosphonate - as a scale inhibitor salt.
2 The material can be added as a fine powder with an
3 average particle size of 1-100µm.
4

5 This capsule was manufactured as detailed for the
6 previous two examples. The inclusion of polyethylene
7 terephthalate in the main matrix material
8 strengthened the bead by a factor of 3 and can be
9 suitable for applications that require the capsule to
10 withstand high pressures. In addition, the inclusion
11 of PET imparts more oil resistance and increase the
12 thermal stability of the product to >180°C. The
13 specific gravity of the material was ~1.3 and it's
14 unconfined compressive strength was >3400psi.
15

16 **Example 5 - Extrusion Temperature 200 - 260°C**
17

18 This capsule was manufactured as detailed for the
19 previous two examples and having 100% Polyamide
20 (Nylon) as the plastic material.
21

22 The use of polyamide as the main matrix material
23 provided even more strength than the bead as quoted
24 in Example 4. The compressive strength was again
25 increased by a factor of 3 and use of Polyamide
26 increases the chemical resistance and thermal
27 stability of the product to >250°C. The material can
28 be suitable for sand control in applications that
29 require the plastic capsule to withstand extremely
30 high pressures and, in addition, the polyamide matrix
31 material can display a slight amount of deformation

1 and can be used for proppant flowback control in
2 hydraulic fractures and gravel packs. Typically this
3 embodiment excludes any substance to be released from
4 the capsule, but can incorporate such substances if
5 desired.

6

7 The specific gravity of this material was ~1.2-1.3
8 and its unconfined compressive strength exceeded
9 12000psi.

10

11 **Example 6** - Extrusion Temperature 200°C -260°C

12

13 This capsule was manufactured as detailed for the
14 previous two examples and has the following
15 proportion of constituents:

16

17 70% Polyamide - as the plastic matrix material. The
18 material can be added as a fine powder with an
19 average particle size of 1-100µm.

20

21 30% Solid Phosphonate - as a scale inhibitor salt.
22 The material can be added as a fine powder with an
23 average particle size of 1-100µm.

24

25 This capsule can be used for sand and proppant flow
26 back control and combined sand/proppant flow back and
27 scale control in gravel packs, fracture packs, screen
28 wells and hydraulic fractures.

29

30 Fig. 2 shows the concentration of scale inhibitor
31 released versus the number of pore volumes of fluid

1 eluted through the packed material. One pore volume
2 is defined here as approximately 25% of the total
3 volume of the packed material and corresponds to the
4 volume in the system that is not occupied by the
5 plastic material. It can be seen from Fig. 2 that
6 the release of scale inhibitor is constant even after
7 6000 pore volumes. Therefore, the scale inhibitor is
8 released at a constant low level for long periods of
9 time.

10

11 It can be seen from Fig. 3 that the material in
12 Example 5 does become slightly strained as the stress
13 is increased to > 8000-10000psi. Therefore a slight
14 amount of deformation of the material does occur in
15 both the presence and absence of scale inhibitor.

16

17 The specific gravity of this material was ~ 1.3 and
18 its unconfined compressive strength was greater than
19 10,500psi.

20

21 **Example 7** - Extrusion Temperature 165°C

22

23 This capsule was manufactured as detailed for the
24 previous two examples and having the following
25 proportion of constituents:-

26

27 40% HDPE (high-density polyethylene) - as the plastic
28 matrix material. The material can be added as a fine
29 powder with an average particle size of 1-100µm.

30

1 30% Barite (barium sulphate) - as the weighting
2 agent. The material can be added as a fine powder
3 with an average particle size of 1-500µm.

4

5 30% solid polycarboxylate - as a scale inhibitor
6 salt. The material can be added as a fine powder with
7 an average particle size of 1-100µm.

8

9 The specific gravity of this material was ~1.3 and
10 its compressive strength was >600psi. The product was
11 also thermally stable in both brine and oil up to
12 between 140°C. The finished capsule is particularly
13 suitable for scale control in rat hole applications.

14

15 **Example 8 - Extrusion Temperature 165°C**

16

17 This capsule was manufactured as detailed for the
18 previous two examples and having the following
19 proportion of constituents:-

20

21 40% HDPE (high-density polyethylene) - as the plastic
22 matrix material. The material can be added as a fine
23 powder with an average particle size of 1-100µm.

24

25 30% Rutile (titanium dioxide) - as the weighting
26 agent. The material can be added as a fine powder
27 with an average particle size of 1-500µm.

28

1 30% solid polycarboxylate - as a scale inhibitor
2 salt. The material can be added as a fine powder
3 with an average particle size of 1-100µm.
4

5 The specific gravity of this material was ~1.3 and
6 its compressive strength was >1000psi. The product
7 displayed similar thermally stability to material in
8 example 7. The finished capsule is particularly
9 suitable for scale control in rat hole applications.
10

11 **Example 9** - Extrusion Temperature 200°C -260°C
12

13 This capsule was manufactured as detailed for the
14 previous two examples and having the following
15 proportion of constituents:-
16

17 65% Polyamide/HDPE (74/16 mix of polyamide/high
18 density polyethylene) - as the plastic matrix
19 material; The material can be added as a fine powder
20 with an average particle size of 1-100µm.
21

22 28% Solid Phosphonate - as a scale inhibitor salt.
23 The material can be added as a fine powder with an
24 average particle size of 1-100µm.
25

26 2% lauric diethanol amine - as an anti static agent.
27 This material can either be added as a liquid or as a
28 fine powder with an average particle size of 1-100µm.
29

1 5% Calcium Stearate - as a lubricant. The material
2 can be added as a fine powder with an average
3 particle size of 1-100µm.

4
5 This capsule can be used for sand and proppant flow
6 back control and combined sand/proppant flow back and
7 scale control in gravel packs, fracture packs, screen
8 wells and hydraulic fractures.

9
10 Figure 4 shows the pore throat size distribution
11 versus the gravel pack compressive stress as
12 determined from a mercury stress injection test (as
13 documented in SPE 8294. It can be seen from Fig. 4
14 that the pore throat size distribution is reduced
15 exponentially with increasing compressive stress,
16 with significant deformation occurring at >3000psi,
17 namely, an 87% reduction in pore throat size and a
18 substantial reduction in permeability to air. The
19 data indicates that at a typical gravel pack
20 compressive stress of 2000psi the product
21 demonstrated acceptable strength characteristics.

22
23 This material can be manufactured down to $500 \pm 25\mu\text{m}$.
24 The specific gravity of this material is ~1.2 and
25 it's confined compressive strength was >2000psi.

26
27 **Example 10** - Extrusion Temperature 165°C - 200°C.

28
29 This capsule was manufactured as detailed for the
30 previous two examples and having the following
31 proportion of constituents:-

1 65% HDPE - as the plastic matrix material; The
2 material can be added as a fine powder with an
3 average particle size of 1-100µm.

4
5 30% Solid Phosphonate - as a scale inhibitor salt.
6 The material can be added as a fine powder with an
7 average particle size of 1-50µm.

8
9 2% lauric diethanol amine - as an anti static agent.
10 This material can be added as a liquid or as a fine
11 powder with an average particle size of 1-100µm.

12
13 3% wax - as a lubricant. This material can be added
14 as a molten liquid or as a fine powder with an
15 average particle size of 1-100µm.

16
17 Figure 5 shows a photomicrograph of a thin section of
18 a gravel pack of the above 300µm material taken from
19 a sand slurry injection test. The sand material was
20 injected as a 1wt%/v slurry at 50ml/minute and the
21 average diameter (D50) of the sand particles was
22 100µm. It can be seen from Fig. 5 that none of
23 injected sand passed into or out of the 300µm gravel
24 pack material. Therefore the above material provided
25 effective sand control at 300µm.

1 This material can be manufactured down to $300 \pm 15\mu\text{m}$.
2 The specific gravity of this material is ~ 1.2 and it
3 is thermally stable in both oil and brine to $>140^\circ\text{C}$.

4
5 **Example 11** - Extrusion Temperature 180°C - 220°C .
6

7 This capsule was manufactured as detailed for the
8 previous two examples and having the following
9 proportion of constituents:-

10
11 70% PolyHydroxyAlkanoate (PHA) - as the degradable
12 polymer matrix material. This material can be added
13 as an agglomerate with an average granule size of 1-3
14 mm.

15
16 30% solid phosphonate - as a scale inhibitor salt.
17 This material can be added as a fine powder with an
18 average particle size of 1- $100\mu\text{m}$.

19
20 The finished capsule is particularly suitable for
21 scale control in rat hole applications. The material
22 has been designed to degrade or slowly dissolve so
23 that it is possible to re-treat the rat hole without
24 the need for expensive remedial cleaning procedures.

25
26 Fig. 6 shows the % weight loss of the total material
27 and scale inhibitor versus the degradation time in
28 days at 107°C . It can be seen from Fig. 6 that the
29 material has undergone a substantial total weight
30 loss. A comparison of the total weight loss with the
31 % mass loss profile due to the release of the

1 encapsulated scale inhibitor, which is relatively
2 constant at a low level, indicated that
3 degradation/dissolution of the polymer matrix was
4 occurring. The trends in the data indicate a
5 predicted degradation lifetime of between 12-14
6 months at 107°C.

7
8 Figure 7 shows the concentration of scale inhibitor
9 released versus the number of cell volumes of brine
10 eluted at 107°C. The test was performed in a
11 specially designed cell to simulate the release of
12 scale inhibitor from a product placed in the rat
13 hole. It can be seen from Fig. 7 that the PHA
14 polymer matrix displays favourable scale inhibitor
15 release characteristics, with the scale inhibitor
16 being released at low levels over a long period.

17
18 The specific gravity of this material was ~1.2-1.3
19 and its compressive strength was >1000psi. The
20 product was also thermally stable in both brine and
21 oil up to between 170-180°C.

22
23 **Example 12** - Extrusion Temperature 200-220°C

24
25 This capsule was manufactured as detailed for the
26 previous two examples and having the following
27 proportion of constituents:-

28
29 61% polyethylene terephthalate(PET) - as the polymer
30 matrix material. This material can be added as a fine
31 powder with an average particle size of 1-100µm.

1 30% solid phosphonate - as a scale inhibitor salt.

2 This material can be added as a fine powder with an
3 average particle size of 1-100µm.

4

5 9% titanium oxide oxidation catalyst - as a
6 degradation additive. This material can be added as
7 a fine powder with an average particle size of 1-
8 100µm.

9

10 The finished capsule is particularly suitable for
11 scale control in rat hole applications. The material
12 has been designed to degrade or slowly dissolve over
13 10-14 months.

14

15 **Example 13** - Extrusion Temperature 165-200°C

16

17 This capsule was manufactured as detailed for the
18 previous two examples and having the following
19 proportion of constituents:-

20

21 55% starch - as the polymer matrix material. This
22 material can be added as a fine powder with an
23 average particle size of 1-100µm.

24

25 35% solid potassium hexacyanoferrate III - as a
26 halite inhibitor salt. This material can be added as
27 a fine powder with an average particle size of 50-
28 500µm.

29

1 10% Tungsten polyamide blend- as a weighting agent.
2 This material can be added as a granule in
3 masterbatch format with an average granule size of
4 500-3000µm.

5
6 The finished capsule is particularly suitable for
7 halite scale control in rat hole applications. The
8 specific gravity of this material was ~1.1-1.3 and
9 the material is thermally stable up to 140°C.

10

11 **Example 14** - Extrusion Temperature 165-200°C

12

13 This capsule was manufactured as detailed for the
14 previous two examples and having the following
15 proportion of constituents:-

16

17 70% polyamide - as the polymer matrix material. This
18 material can be added as a fine powder with an
19 average particle size of 1-100µm.

20

21 30% solid enzyme - as the acid generating enzyme.
22 This material can be added as a granule with an
23 average particle size of 100-1000µm.

24

25 This material is suitable for sand control and
26 improved well clean up after completion in both
27 injection and production wells.

28

29 Modifications and improvements may be incorporated
30 without departing from the scope of the invention.

1 Claims

2

3 1. A substance release device comprising a
4 polymeric material for releasing a substance
5 into a downhole fluid environment in a well.

6

7 2. A device according to claim 1, wherein the
8 substance comprises one or more selected from
9 the group comprising scale inhibitors, hydrate
10 and halite inhibitors, corrosion inhibitors,
11 biocides, wax and asphaltene control substances,
12 demulsifiers, gel breakers, tracers, drag
13 reducers and well clean up substances including
14 enzymes; organic molecules, acids, esters, and
15 aliphatic substances.

16

17 3. A device as claimed in any preceding claim
18 wherein the polymeric material is permeable.

19

20 4. A device as claimed in any preceding claim,
21 wherein the material is one or more selected
22 from the group comprising polypropylene,
23 polyethylene, high density polyethylene, high
24 density polypropylene, polyethylene
25 terephthalates, polyamides (both aliphatic and
26 aromatic), liquid crystal polymers, liquid
27 engineered resins, starch and polyhydroxy
28 alkanoates or mixtures of these.

29

30 5. A device as claimed in any preceding claim,
31 wherein the material comprises a matrix that

1 provides the material with structural support,
2 and which contains the substance to be released.

3
4 6. A device as claimed in claim 5, wherein the
5 material also contains one or more of the group
6 of substances comprising acrylic, polybutylene,
7 polycarbonate, polyester, polystyrene,
8 polyurethane, polyvinyl chloride,
9 polycaprolactone, polybutylene terephthalate,
10 polyvinyl alcohol, polylactic acid,
11 polyglycolide, polyester amide, polyimides,
12 acrylonitrile-butadiene-styrene, acrylonitrile-
13 styrene-acrylate, polyoxymethylene,
14 polybutylene, polyisobutylene, polyvinylbutyral,
15 epichlorohydrin elastomer, nitrile elastomer,
16 nitrile rubber, polyetherketone,
17 polyetheretherketone, polyetherketoneketone,
18 polymethylmethacrylate, polyethylene oxide,
19 polyphenylene oxide, polysulphones,
20 polyethersulphone, polyurea, chlorinated
21 polyethylene, ethylene-chlorofluoroethylene,
22 tetrafluoroethylene-perfluoropropylene,
23 Perfluoroalkoxy, silicon rubbers and other
24 polymeric materials consisting of mixtures of
25 these, copolymers, terpolymers and
26 hydrophobically/hydrophilically modified and
27 crosslinked derivatives of these.

28
29 7. A device as claimed in any preceding claim,
30 wherein the material contains one or more of the
31 group of substances comprising waxes, calcium

- 1 stearate, metallocene, thermoplastic rubber,
2 resins, hot melt adhesives, fibreglass,
3 silicones, fluorosilicones e.g. Ryton,
4 polysiloxanes, fluoroelastomers e.g. Viton,
5 Aflas, fluorocarbons e.g. PTFE, PVDF,
6 halogenated polymers, cellulose,
7 polysaccharides, lignin, chitin, gums and
8 mixtures and derivatives of the above.
9
- 10 8. A device as claimed in any preceding claim,
11 comprising a generally spherical capsule.
12
- 13 9. A device as claimed in any preceding claim,
14 manufactured using an underwater pelletising
15 system using an extrusion and either a
16 spheronisation or granulation process.
17
- 18 10. A device as claimed in any preceding claim,
19 wherein the material contains a high active
20 content of substance to be released.
21
- 22 11. A device as claimed in any preceding claim,
23 including a weighting agent to adjust the
24 density of device.
25
- 26 12. A device as claimed in claim 11, wherein the
27 weighting agent is selected from the group
28 comprising barite, zirconium oxide, manganese
29 oxide, titanium dioxide, tungsten and magnetite.
30

- 1 13. A device as claimed in any preceding claim,
2 including a strengthening agent to adjust the
3 hardness, compressive strength and/or elastic
4 properties of the device.
5
- 6 14. A device as claimed in claim 13, wherein the
7 strengthening agent is selected from the group
8 comprising glass, sand, minerals, carbon fibres,
9 boron fibres and impact modifiers.
10
- 11 15. A device as claimed in any preceding claim,
12 wherein the material has a specific gravity
13 between 0.9 and 2.0.
14
- 15 16. A device as claimed in any one of claims 1-14,
16 wherein the device has a specific gravity up to
17 12.
18
- 19 17. A device as claimed in any preceding claim,
20 wherein the device and/or the material is
21 pliable.
22
- 23 18. A method of treating a well, the method
24 comprising loading a substance into a polymeric
25 material, inserting the material into the well,
26 and allowing the substance to leach from the
27 polymeric material into the well.
28
- 29 19. A method as claimed in claim 18, wherein the
30 substance comprises one or more selected from
31 the group comprising scale inhibitors, corrosion

1 inhibitors, hydrate and halite inhibitors,
2 biocides, wax and asphaltene control substances,
3 demulsifiers, gel breakers, tracers, drag
4 reducers and well clean up substances, enzymes,
5 organic molecules, acids, esters, copolymers,
6 ter-polymers, aliphatic compounds, polymeric
7 species, and other oilfield production
8 chemicals.

9

10 20. A method according to claim 18 or claim 19,
11 wherein the material releases well cleanup
12 substances.

13

14 21. A method as claimed in any one of claims 18-20,
15 wherein the material is inserted into a fissure,
16 fracture, screen area, gravel pack, fracture
17 pack or a pre-packed screen.

18

19 22. A method as claimed in any one of claims 18-21,
20 wherein the material is injected into the
21 rathole or base of a well.

22

23 23. A method as claimed in any one of claims 18-22,
24 wherein the material is used to support portions
25 of the well, reservoir or formation in addition
26 to releasing the substance.

27

28 24. A method according to any one of claims 18-23,
29 wherein the material controls entry of
30 particulate matter into the production stream of
31 the well.

- 1 25. A method as claimed in any one of claims 18-24,
2 wherein the material is loaded with a high
3 active content of the substance to be released.
4
- 5 26. A method as claimed in any one of claims 18-25,
6 wherein the solubility of the substance is
7 selected to suit prevailing well conditions.
8
- 9 27. A method as claimed in any one of claims 18-26,
10 wherein the hardness of the material is adjusted
11 to suit prevailing well conditions.
12
- 13 28. A method as claimed in any one of claims 18-27,
14 wherein the oil and/or acid tolerance of the
15 material is adjusted to suit prevailing well
16 conditions.
17
- 18 29. A method as claimed in any one of claims 18-28,
19 wherein a number of the devices having a
20 generally heterogeneous size distribution are
21 delivered to the well.
22
- 23 30. A method as claimed in any one of claims 18-28,
24 wherein a number of the devices having a
25 generally homogeneous size distribution are
26 delivered to the well.
27
- 28 31. A method as claimed in claim 30, wherein the
29 size distribution of devices delivered to the
30 well is $\pm 5\%$ of the mean size.
31

- 1 32. A method as claimed in any one of claims 29-31,
2 wherein the range of sizes of the devices
3 delivered to the well is 250µm - 5mm.
4
- 5 33. A method as claimed in any one of claims 18-32,
6 wherein the material is adapted to degrade over
7 a period of time, after which the well is re-
8 treated.
9
- 10 34. A method as claimed in claim 33, wherein the
11 period of degradation is adjusted to suit the
12 prevailing well conditions.
13
- 14 35. A method as claimed in any one of claims 18-34,
15 wherein the rate and lifetime of release of the
16 substance is adjusted to suit the degradation
17 lifetime of the material.
18
- 19 36. A method as claimed in any one of claims 18-35,
20 wherein the material is charged with one or more
21 substances selected from the group comprising
22 scale inhibitors, hydrate and halite inhibitors,
23 corrosion inhibitors, biocides, wax and
24 asphaltene control substances, demulsifiers, gel
25 breakers, tracers, drag reducers and well clean
26 up substances including enzymes; organic
27 molecules, acids, esters, and aliphatic
28 substances.
29
- 30 37. A method of forming a substance-releasing
31 particle for release of substances into a fluid

1 environment in an well, the method comprising
2 mixing the substance to be released with a
3 matrix material forming the particle, and
4 thereafter forming the particle from the mixture
5 of the matrix and the substance, so that the
6 substance is dispersed throughout the formed
7 particle.
8

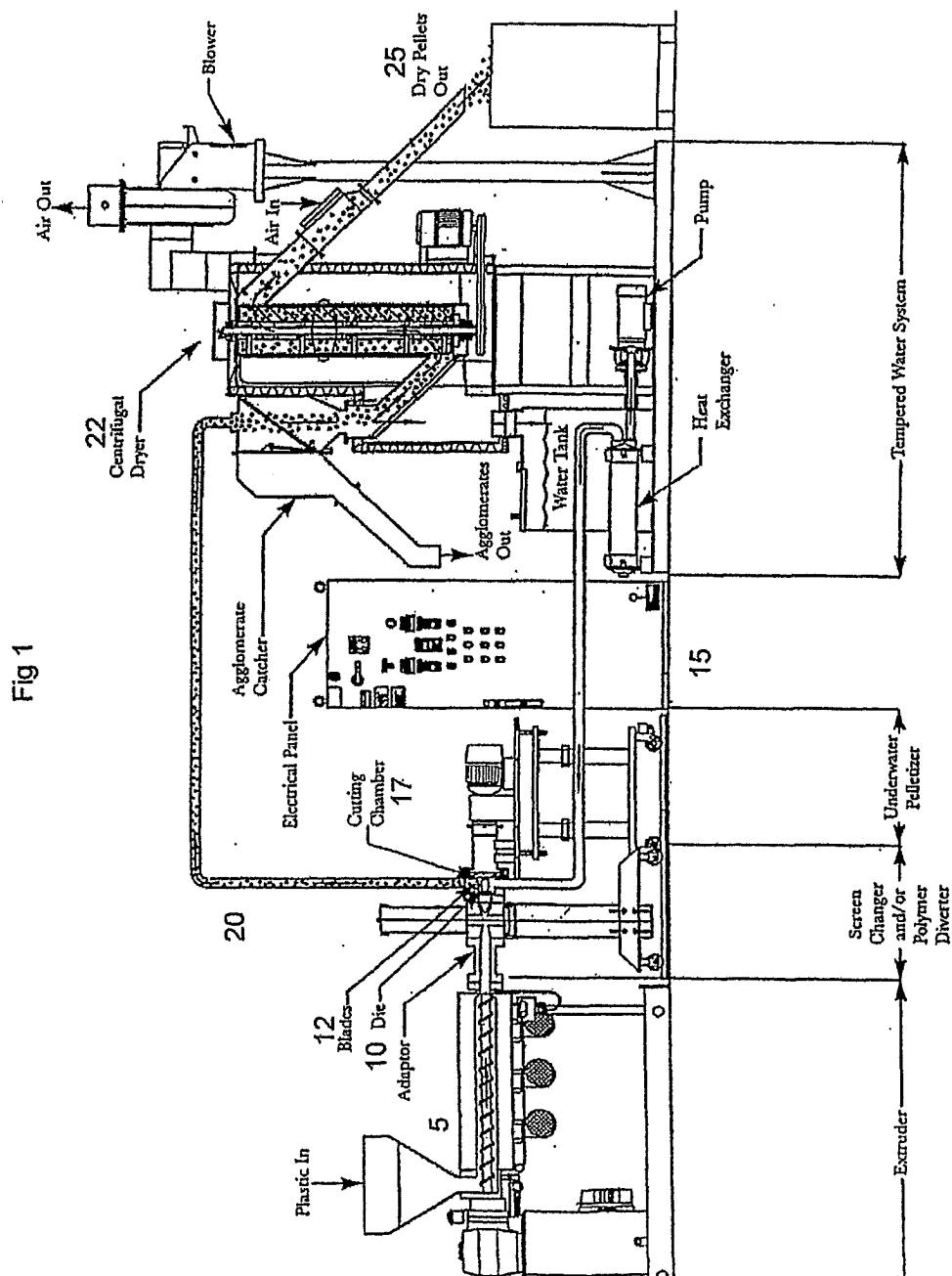
9 38. A polymeric downhole proppant.
10

11 39. A method of supporting a well or a portion
12 thereof, comprising disposing a support material
13 in the well or portion to be supported, wherein
14 the support material comprises a polymeric
15 material.
16

17 40. A polymeric material for use downhole for the
18 control of particulate matter entering the
19 production stream of the well.
20

21 41. A method of controlling the entry of particulate
22 matter into the production stream of a well, the
23 method comprising disposing a number of
24 polymeric devices into the wellbore between the
25 formation and the production fluids outlet of
26 the well.

1/5



2/5

Fig 2 -- Scale Inhibitor Release Profile from a Plastic Capsule

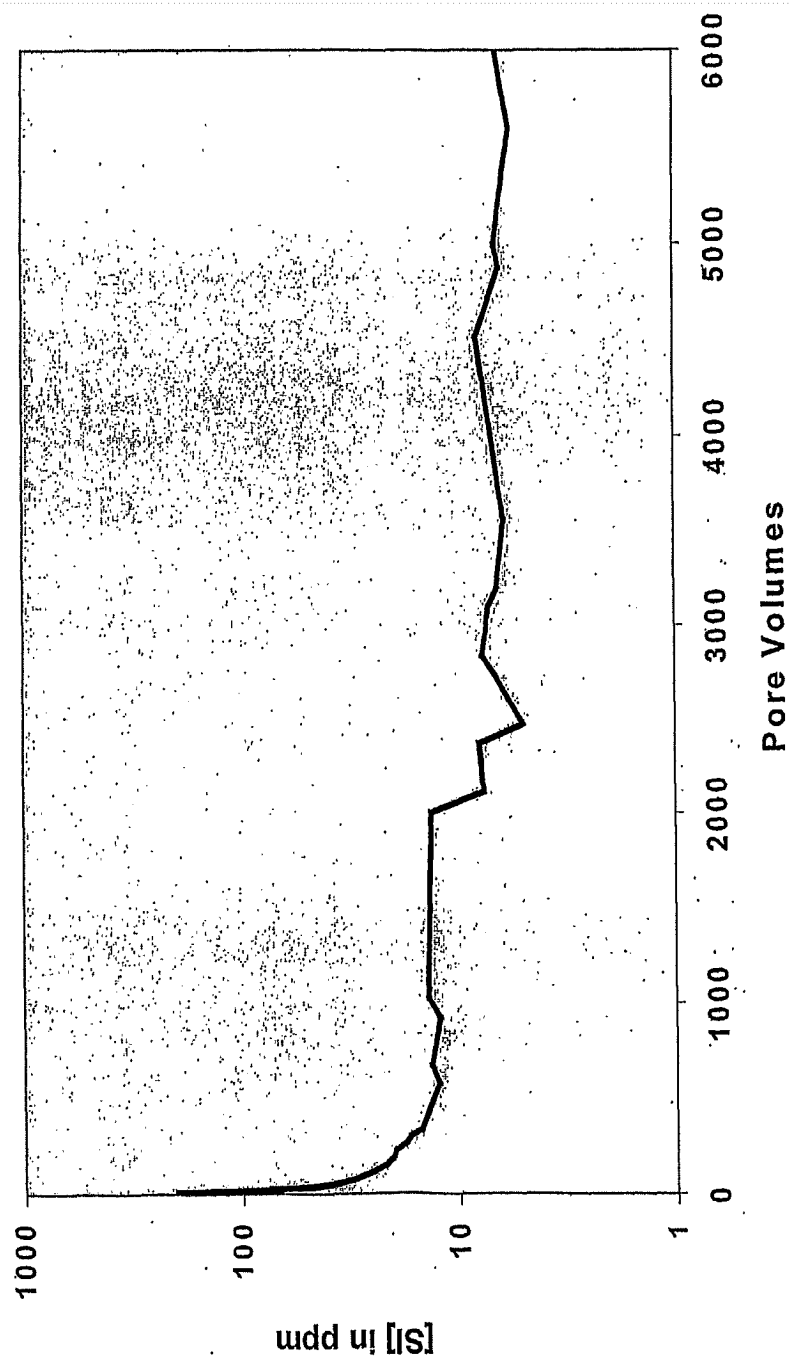


Fig 3

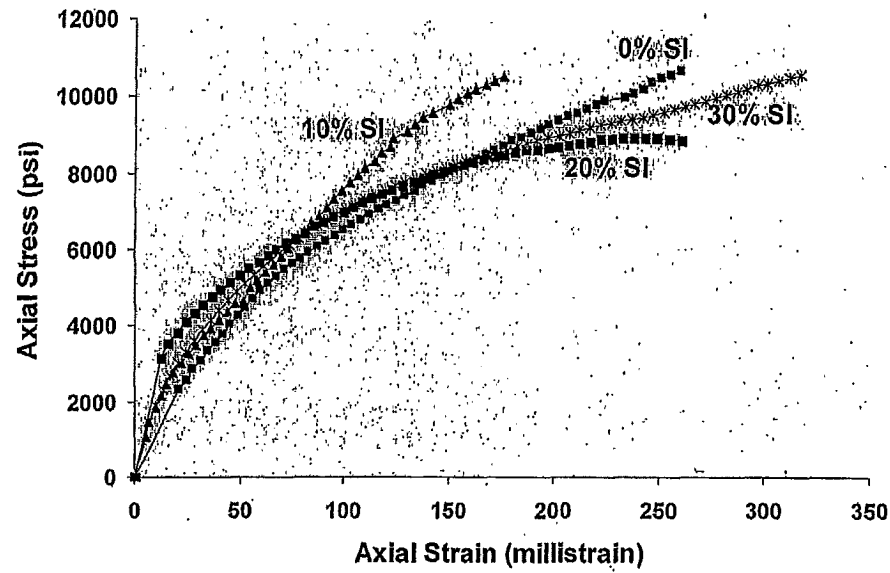
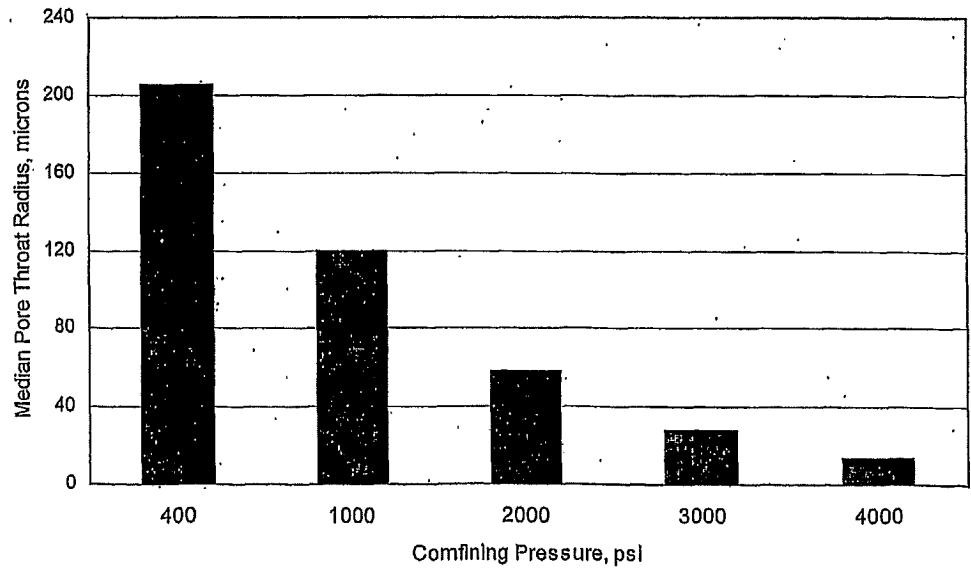


Fig 4



4/5

Fig 5

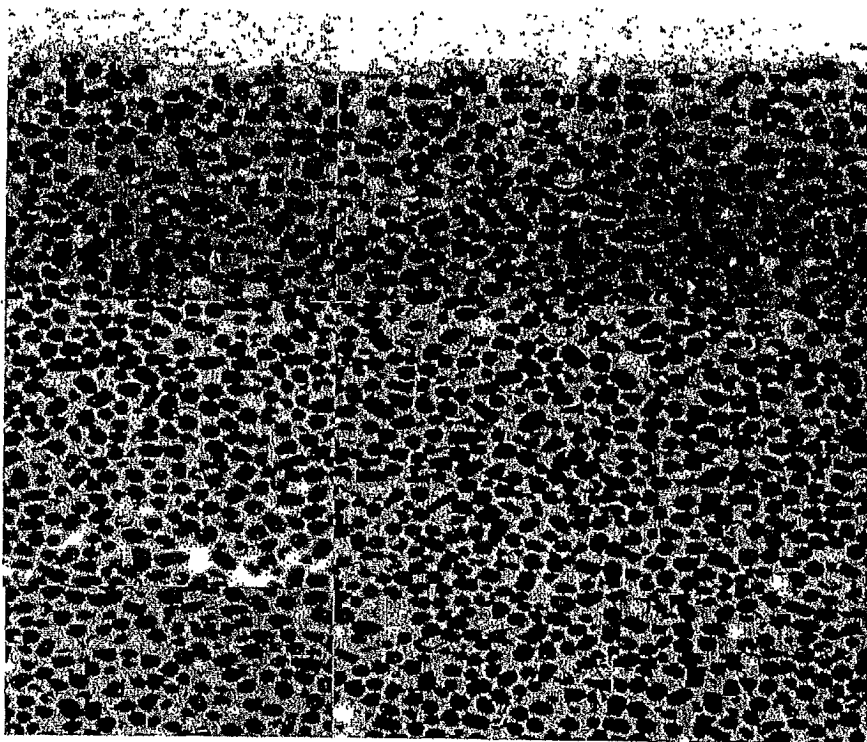
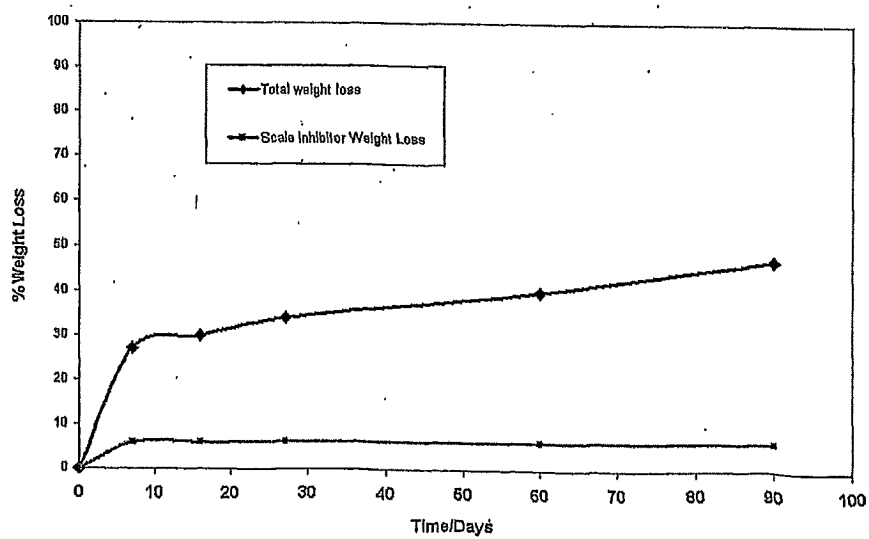
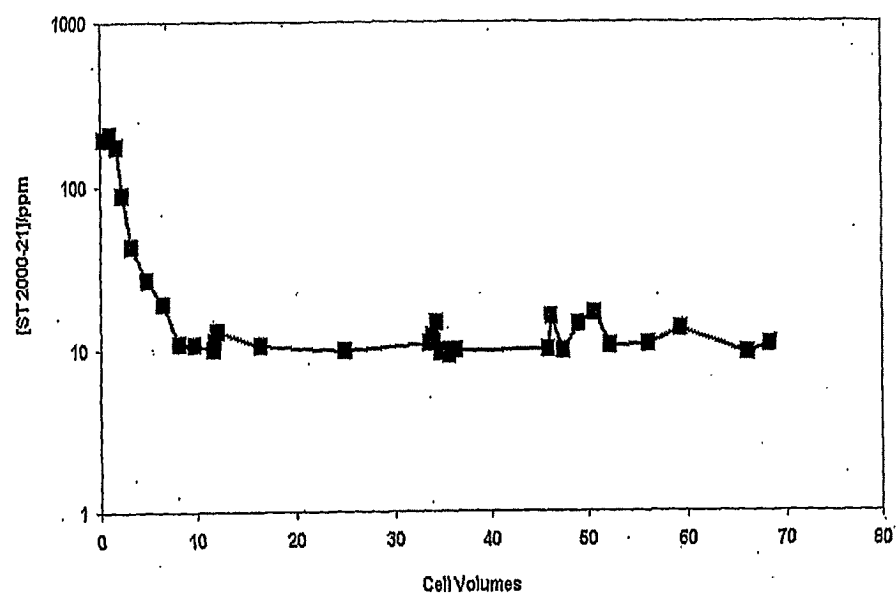


Fig 6



5/5

Fig 7



INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/GB 01/02482

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 E21B37/06 E21B43/25 E21B41/02 E21B43/267

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 E21B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 738 897 A (MCDUGALL ET AL.) 19 April 1988 (1988-04-19) column 2, line 50 - column 3, line 2 column 8, line 13 - line 19 column 8, line 40 - line 44 column 9, line 1 - line 5 ---	1-3, 5, 18, 19, 21, 33, 36, 37
X	US 3 659 651 A (GRAHAM) 2 May 1972 (1972-05-02) column 1, line 66 - column 2, line 12 --- -/--	38-41

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

27 September 2001

Date of mailing of the international search report

04/10/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rampelmann, K

INTERNATIONAL SEARCH REPORT

Int lional Application No

PCT/GB 01/02482

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 059 034 A (RICKARDS ET AL.) 9 May 2000 (2000-05-09) column 14, line 1 - line 24 column 17, line 10 - line 32 column 18, line 21 - line 24 column 20, line 57 - column 21, line 3	39-41
A	----	17,23
X	US 5 922 652 A (KOWALSKI ET AL.) 13 July 1999 (1999-07-13) column 3, line 38 - line 43 column 5, line 13 - line 33 column 7, line 11 - line 35	1,2,5, 10-12, 18,19
X	US 4 986 354 A (CANTU) 22 January 1991 (1991-01-22) claim 1	1,18
X	US 4 741 401 A (WALLES ET AL.) 3 May 1988 (1988-05-03) claims 15,29	1,2,20
A	EP 0 919 695 A (FRACMASTER LTD.) 2 June 1999 (1999-06-02) page 4, line 15 - line 16	3
A	US 5 893 416 A (READ) 13 April 1999 (1999-04-13) column 2, line 19 - line 36	5,13,14
A	US 3 676 363 A (MOSIER) 11 July 1972 (1972-07-11) column 2, line 9 - line 14 column 2, line 72 - line 75 column 3, line 60 - line 72 column 6, line 17 - line 27 column 6, line 52 - line 72	8,11,22, 24,33-36
X,P	US 6 207 620 B1 (GONZALEZ ET AL.) 27 March 2001 (2001-03-27) column 5, line 50 - column 6, line 4 column 7, line 7 - line 30 column 7, line 43 - line 45 claim 1	1,2,6,7, 9,10,18, 19,21, 25,27-32

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/02482

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4738897	A	19-04-1988	US 4670166 A AU 583095 B2 AU 5409286 A CA 1262507 A1 DE 3673190 D1 EP 0193369 A2 NO 860713 A ,B,	02-06-1987 20-04-1989 04-09-1986 31-10-1989 13-09-1990 03-09-1986 28-08-1986
US 3659651	A	02-05-1972	NONE	
US 6059034	A	09-05-2000	AU 7600198 A GB 2348907 A WO 9927229 A1 DK 133397 A GB 2359316 A GB 2319796 A ,B NL 1007616 C2 NL 1007616 A1 NO 975440 A	15-06-1999 18-10-2000 03-06-1999 28-05-1998 22-08-2001 03-06-1998 18-01-2000 28-05-1998 28-05-1998
US 5922652	A	13-07-1999	AT 149237 T AU 4227493 A BR 9306321 A CA 2134980 A1 CZ 9402703 A3 DE 69308297 D1 EP 0639240 A1 FI 945196 A HU 70884 A2 JP 7506408 T NO 944206 A NZ 252502 A RU 2111049 C1 SK 132294 A3 WO 9322537 A1	15-03-1997 29-11-1993 26-03-1996 11-11-1993 14-06-1995 03-04-1997 22-02-1995 04-11-1994 28-11-1995 13-07-1995 04-11-1994 29-01-1997 20-05-1998 11-07-1995 11-11-1993
US 4986354	A	22-01-1991	NONE	
US 4741401	A	03-05-1988	AU 582320 B2 AU 1023188 A BR 8800186 A CA 1274767 A1 CN 88100379 A ,B GB 2199872 A ,B IN 170553 A1 MX 172677 B NO 177199 B	16-03-1989 25-08-1988 30-08-1988 02-10-1990 02-11-1988 20-07-1988 11-04-1992 07-01-1994 24-04-1995
EP 919695	A	02-06-1999	AU 9410098 A EP 0919695 A2 NO 985482 A US 6184184 B1	17-06-1999 02-06-1999 26-05-1999 06-02-2001
US 5893416	A	13-04-1999	DE 69426970 D1 DE 69426970 T2 DK 656459 T3 EP 0656459 A1 GB 2284223 A ,B	03-05-2001 13-09-2001 18-06-2001 07-06-1995 31-05-1995

INTERNATIONAL SEARCH REPORT
Information on patent family members

Int lonal Application No
PCT/GB 01/02482

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5893416 A		JP 7197764 A NO 944512 A	01-08-1995 29-05-1995
US 3676363 A	11-07-1972	NONE	
US 6207620 B1	27-03-2001	AU 5455200 A WO 0075486 A1	28-12-2000 14-12-2000